

Pressure-induced Phonon Softenings and the Structural and Magnetic Transitions in CrO_2

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To investigate the pressure-induced structural transitions of chromium dioxide (CrO_2), phonon dispersions and total energy band structures are calculated as a function of pressure. The first structural transition has been confirmed at $P \approx 10$ GPa from the ground state tetragonal CrO_2 (t- CrO_2) of rutile type to orthorhombic CrO_2 (o- CrO_2) of CaCl_2 type. The half-metallic property is found to be preserved in o- CrO_2 . The softening of Raman-active B_{1g} phonon mode, which is responsible for this structural transition, is demonstrated. The second structural transition is found to occur for $P \geq 61.1$ GPa from ferromagnetic (FM) o- CrO_2 to nonmagnetic (NM) monoclinic CrO_2 (m- CrO_2) of MoO_2 type, which is related to the softening mode at $\mathbf{q} = R(\frac{1}{2}, 0, \frac{1}{2})$. The third structural transition has been newly identified at $P = 88.8$ GPa from m- CrO_2 to cubic CrO_2 of CaF_2 type that is a FM insulator.

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I. INTRODUCTION

Chromium dioxide (CrO_2), which crystallizes in the tetragonal structure of rutile-type, is a well-known material because of its half-metallic nature with $T_c = 390$ K.¹ The origin of the ferromagnetic (FM) and half-metallic property of CrO_2 was explained in terms of the double-exchange model.^{2,3} Due to the crystal field of distorted (flattened) CrO_6 octahedra, Cr t_{2g} states are split into lower d_{xy} and higher d_{xz}/d_{yz} states. Out of two d electrons of Cr^{4+} , one occupies the lower d_{xy} that is localized, while the other occupies the higher d_{xz}/d_{yz} that are delocalized near the Fermi level (E_F) due to the hybridization with O p states. Then the double-exchange interaction arises from the Hund coupling between localized d_{xy} and delocalized half-filled d_{xz}/d_{yz} states, so as to produce the FM and half-metallic properties.

In contrast to numerous reports on electronic and magnetic properties of CrO_2 , there have been relatively small number of studies on structural and lattice dynamical properties of CrO_2 . Especially, there is no experimental or theoretical report on the phonon dispersion curve for CrO_2 , except for a few Raman studies.⁴⁻⁶ Under the pressure, CrO_2 is known to undergo the structural transition from the ground state tetragonal CrO_2 (t- CrO_2) to the orthorhombic CrO_2 (o- CrO_2) of CaCl_2 -type at $P = 12$ -14 GPa.^{4,7} The question followed is whether there will an additional structural transitions from o- CrO_2 at higher pressure. In fact, this question is not just for CrO_2 but also relevant to the structural stability issue of transition-metal (TM) dioxides (TMO_2). Note that TMO_2 s show diverse structures depending on the TM elements.⁸⁻¹¹ Furthermore, magnetic properties of CrO_2 under the pressure are intriguing, such as (i) whether the half-metallic nature is preserved, and (ii) when CrO_2 becomes non-magnetic.

In this work, to investigate the pressure-induced structural transitions of CrO_2 , we have studied phonon dispersions and total energies of relevant CrO_2 structures as a

function of pressure. Based on the calculated phonon dispersions and the total energies, we have found three possible structural transitions with increasing pressure. The first transition is consistent with the known transition from t- CrO_2 to o- CrO_2 . At this transition, FM and half-metallic properties are preserved, in agreement with previous reports of literature.^{4,7} The second transition is from o- CrO_2 to monoclinic CrO_2 (m- CrO_2) of MoO_2 type, which is nonmagnetic (NM). The third transition is identified from m- CrO_2 to cubic CrO_2 (c- CrO_2) of CaF_2 -type. Interestingly, c- CrO_2 is a FM insulator even at the high pressure of $P \geq 88.8$ GPa. Note that the second and third structural transitions are our new findings for CrO_2 under the high pressure.

II. COMPUTATIONAL DETAILS

Band structures and phonon dispersions of CrO_2 were obtained by employing the pseudo-potential band method and the linear response method, respectively, implemented in the Quantum ESPRESSO code.^{12,13} The generalized gradient approximation (GGA) is utilized for the exchange-correlation potential. Self-consistent electron and phonon band calculations were carried out after the full-relaxation of internal atomic positions and lattice parameters.

We have considered various structures of CrO_2 . At the ambient pressure, the stable phase is t- CrO_2 of rutile-type ($P4_2/mnm$), in which Cr atoms are positioned at (0,0,0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, while O atoms at $\pm(u, u, 0)$ and $\pm(\frac{1}{2}+u, \frac{1}{2}-u, \frac{1}{2})$. Initial lattice constants and atomic positions adopted before the full-relaxation are $a=b=4.421\text{\AA}$, $c=2.916\text{\AA}$, and $u=0.3043$.¹⁴ For the high pressure phase of o- CrO_2 of CaCl_2 -type ($Pnnm$), we have adopted $a=4.3874\text{\AA}$, $b=4.2818\text{\AA}$, $c=2.8779\text{\AA}$, $u_x=0.299$, and $u_y=0.272$.⁴ For candidate structural phases at the higher pressure, we considered m- CrO_2 of MoO_2 type ($P2_1/c$)^{10,11} and c- CrO_2 of CaF_2 -type ($Fm\bar{3}m$).¹⁵ In the

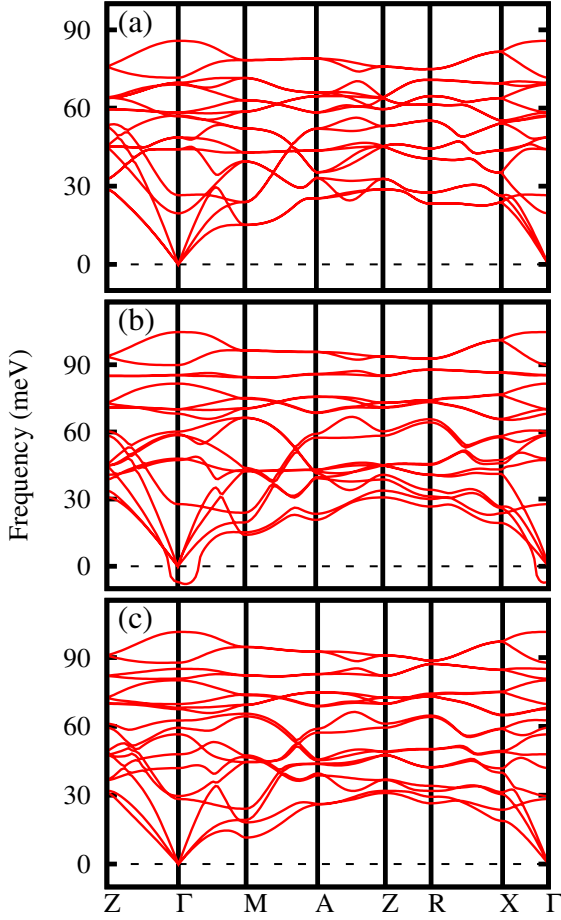


FIG. 1: (Color online) The phonon dispersion curves of CrO_2 . (a) FM t-CrO_2 of rutile type at the ambient pressure. (b) FM t-CrO_2 at $P=34.0$ GPa. Notice the phonon softening at Γ , which corresponds to the B_{1g} mode. The negative frequency here represents the imaginary part of the phonon frequency. (c) FM o-CrO_2 of CaCl_2 type at $P=34.1$ GPa.

latter, a Cr atom is positioned at $(0, 0, 0)$, and O atoms at $(0.25, 0.25, 0.25)$, $(0.25, 0.25, 0.75)$.

III. RESULTS

Figure 1 shows the phonon dispersions of t-CrO_2 and o-CrO_2 at the ambient and high pressures. As shown in Fig. 1(a), t-CrO_2 at the ambient pressure has regular phonon dispersions, reflecting the stable phase of t-CrO_2 at the ambient pressure. In contrast, t-CrO_2 at $P=34.0$ GPa in Fig. 1(b) has a softening phonon mode at $\mathbf{q}=\Gamma$, indicating the structural instability of t-CrO_2 at this pressure. The softened mode corresponds to B_{1g} mode that is Raman-active. As shown in Fig. 2, B_{1g} mode generates the rotating motions of oxygen ions. The resulting

lattice displacements induce the structural transformation from t-CrO_2 of rutile type to o-CrO_2 of CaCl_2 type. Figure 1(c) provides the phonon dispersion of o-CrO_2 at $P=34.1$ GPa. The phonon dispersion is regular, implying that o-CrO_2 is stable at this pressure. Therefore, Fig. 1 clearly demonstrates that there is a structural transition from t-CrO_2 to o-CrO_2 at the pressure of $P \leq 34$ GPa.

In Fig. 3(a), we plotted the calculated Raman-active phonons of t-CrO_2 and o-CrO_2 as a function of pressure. There are four Raman modes (B_{1g} , E_g , A_{1g} , B_{2g}) for t-CrO_2 , and six Raman modes (A_g , B_{1g} , B_{2g} , B_{3g} , A_g , B_{1g}) for o-CrO_2 .^{6,16,17} Our data are consistent with experimental data up to $P \approx 40$ GPa.⁴ With increasing the pressure, one can clearly see the softening of B_{1g} mode of t-CrO_2 , which indicates the structural instability of t-CrO_2 . One can also notice two transition points. The first one corresponds to the transition from t-CrO_2 to o-CrO_2 at $P=9.8$ GPa. At this transition, CrO_2 keeps its FM and half-metallic properties.^{4,7,15} The second one corresponds to the transition at $P=76.0$ GPa. The stable structure for $P \geq 76$ has not been identified yet.

The phonon anomalies at two transition points are also revealed in the variation of lattice constants of CrO_2 under the pressure. In Fig. 3(b), the lattice constants are plotted as a function of pressure. One can see anomalous behaviors of the lattice constants at the two transition points that are coincident with those in Fig. 3(a).

To investigate the second structural transition in more detail, we have examined the behavior of magnetic moment. Srivastava *et al.*¹⁵ once reported that there would be a magnetic transition in t-CrO_2 from half-metallic to NM at $P \approx 65$ GPa. However, as discussed above, there occurs a structural transition from t-CrO_2 to o-CrO_2 at the low pressure of about $P=10$ GPa. Hence, in Fig. 4(a), we have examined the magnetic moment behavior for o-CrO_2 . It is seen that there is a FM to NM transition at $P=76.0$ GPa, which is close to the second structural transition point.

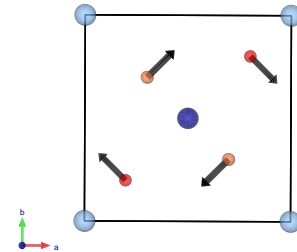


FIG. 2: (Color online) The normal mode of the B_{1g} soft phonon at Γ for $P=34.0$ GPa. The blue and light-blue circles represent Cr ions, while the orange and red circles represent oxygen ions. Blue and orange ions are located at $z=\frac{1}{2}$. Only the oxygen ions move in this mode.

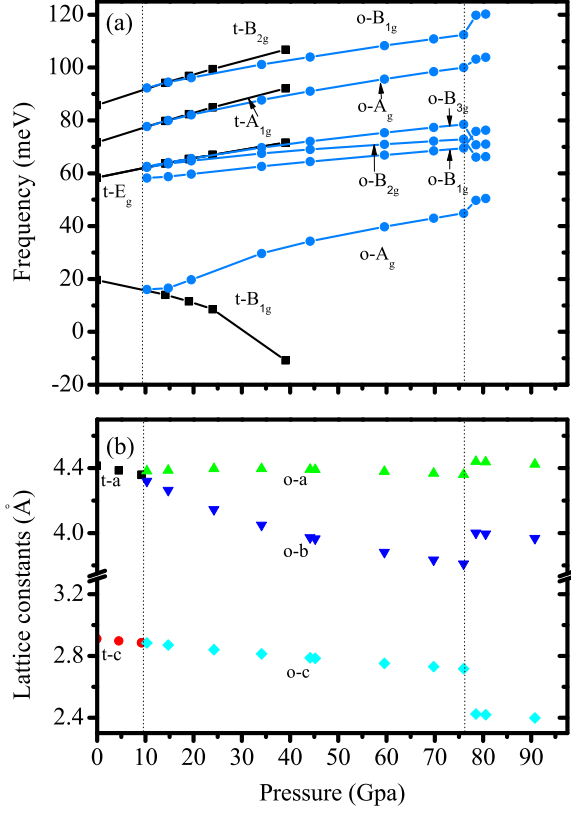


FIG. 3: (Color online) (a) Calculated Raman-active phonon frequencies of t-CrO₂ and o-CrO₂ versus pressure. t- and o- stand for t-CrO₂ and o-CrO₂ respectively. The lines connecting data are guide for eyes. Two phase transitions are noticed at P=9.8 GPa and P=76.0 GPa, which are marked by vertical lines. (b) Calculated equilibrium lattice constants of t-CrO₂ and o-CrO₂ versus pressure.

The magnetic moment of o-CrO₂ suddenly drops at this transition point. The half-metallic property persists up to this pressure. This magnetic transition was also observed by Kuznetsov *et al.*⁷, who obtained the transition pressure of P=53 GPa based on the pseudo-potential band method implemented in the VASP code.

It is thus tempting to conjecture that the second transition observed in Fig. 3(a) corresponds to the magnetic transition in o-CrO₂. However, the phonon dispersion curve in Fig. 4(b) for NM o-CrO₂ at P=80.5 GPa shows the strong phonon softenings, indicating that even NM o-CrO₂ is unstable at the pressure of P> 76.0 GPa. Therefore, it is not possible that FM o-CrO₂ changes into NM o-CrO₂ with increasing the pressure. There might be an additional structural transition in this pressure range.

Two candidate structures after the transition are m-CrO₂ of MoO₂ type and c-CrO₂ of CaF₂ type. The monoclinic structure of MoO₂ type is chosen from the expectation that, with increasing pressure, two *d* electrons of Cr become itinerant, and the local environment

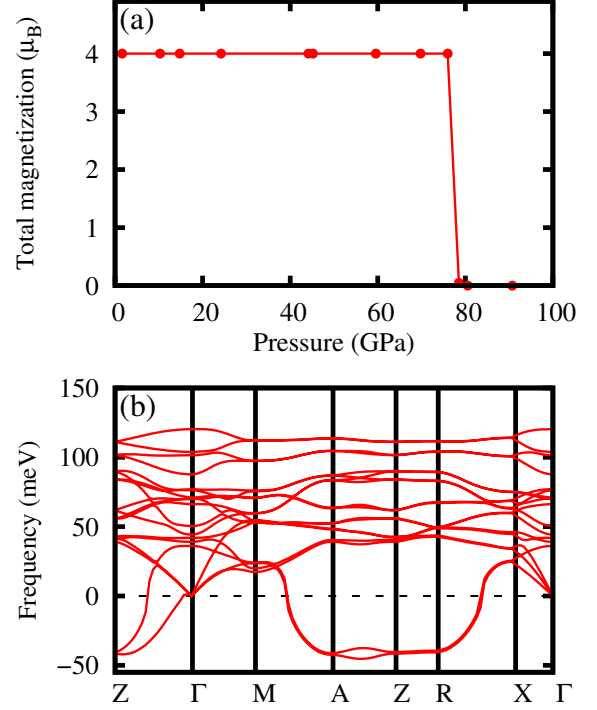


FIG. 4: (Color online) (a) Calculated magnetic moment of o-CrO₂ versus pressure. Magnetic transition from the FM to the NM phase occurs at P=76.0 GPa. (b) The phonon dispersion curve of NM o-CrO₂ at P=80.5 GPa.

becomes similar to that of MoO₂. In a similar system VO₂, a softening of phonon frequency was observed at $\mathbf{q}=\mathbf{R}$ ($\frac{1}{2}, 0, \frac{1}{2}$), which corresponds to the atomic movements from the tetragonal structure of rutile-type to the monoclinic structure.¹⁸ Indeed, the softening mode at $\mathbf{q} = \mathbf{R}$ in Fig. 4(b) is related to this structural transition, because the orthorhombic structure of CaCl₂ type is nothing but the distorted rutile-type structure. Figure 5 depicts the normal mode of the softened phonon mode at $\mathbf{q} = \mathbf{R}$. The displacements generate Cr-Cr dimerization along the *c*-axis, which is consistent with the main

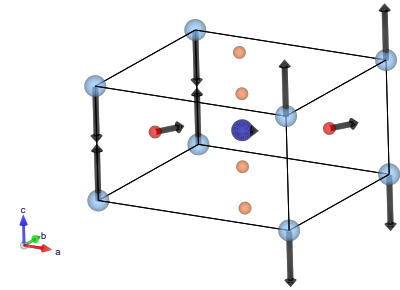


FIG. 5: (Color online) The normal mode of the softened phonon at $\mathbf{q} = \mathbf{R}$ for P=80.5 GPa. The blue and light-blue circles represent Cr ions, while the orange and red circles represent oxygen ions.

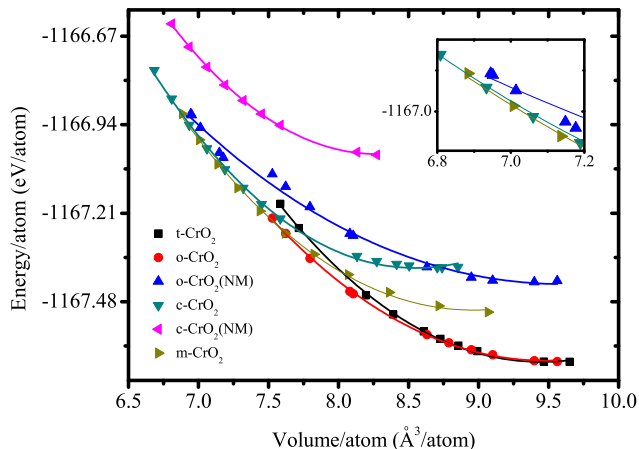


FIG. 6: (Color online) Total energies of various CrO_2 structures versus volume. Data are fitted by the Birch-Murnaghan equation of state.

distortions of the transition from the rutile-type to the monoclinic structure. It is thus reasonable to expect the second transition to be from o-CrO_2 of CaCl_2 type to m-CrO_2 of MoO_2 type. Concerning another candidate, c-CrO_2 of CaF_2 type, there were previous reports predicting the structural transitions from CaCl_2 type to CaF_2 type structure for CrO_2 ¹⁵ and RuO_2 .¹⁹ Also, CaF_2 type is a typical structure of TMO_2 . For example, ZrO_2 and HfO_2 , which have relatively large cations, crystallize in CaF_2 type structure at high temperature.²⁰

To identify the additional structural transition at the higher pressure, we have compared the total energies of candidate structures in Fig. 6. From the total energy versus volume curves in Fig. 6, one can identify three structural phase transitions. The first one is from FM t-CrO_2 to FM o-CrO_2 at the estimated pressure of $P=12.2$ GPa, which is consistent with phonon calculation in Fig. 3. For $P \geq 61.1$ GPa, NM m-CrO_2 becomes the most stable, which corresponds to the second transition from o-CrO_2 to m-CrO_2 , as discussed in the phonon study of Fig. 4. For $P \geq 88.8$ GPa, c-CrO_2 , which is a FM insulator, becomes the most stable. The more stable FM and insulating phase than the NM metallic phase of c-CrO_2 at this high pressure is extraordinary. The magnetic moment of c-CrO_2 amounts to $\sim 2\mu_B/\text{Cr}$, which is close

to those in t-CrO_2 and o-CrO_2 . Note, however, that c-CrO_2 is an insulator not a half-metal. We have confirmed this result by employing the all-electron full potential linearized augmented plane wave method (FLAPW) band method²¹ implemented in WIEN2k package too.²² The present result is different from that by Srivastava *et al.*,¹⁵ who obtained the stable NM metallic phase of c-CrO_2 for $P > 90$ GPa. The different result is likely to come from their use of a simple tight-binding LMTO band method.

The transition from m-CrO_2 to c-CrO_2 is thought to originate from the increasing packing ratio. There are six and eight oxygens around Cr in m-CrO_2 and c-CrO_2 , respectively. Haines *et al.*¹⁹ proposed several possible paths of structural transition from rutile to CaF_2 type structure in TMO_2 . Interestingly, one of the paths is the same as the present structural transition path, rutile-type ($P4_2/mnm$) \rightarrow CaCl_2 -type ($Pnmm$) \rightarrow MoO_2 -type ($P2_1/c$) \rightarrow CaF_2 -type ($Fm\bar{3}m$). But they did not take into account the magnetic state.

IV. CONCLUSION

We have studied the pressure effect on the structural properties of CrO_2 by performing the phonon dispersion and total energy band structure calculations. Combining two analysis methods, we have found that there are three structural transitions with increasing pressure up to 100 GPa. The first one is the transition from t-CrO_2 of rutile type to o-CrO_2 of CaCl_2 type at $P \approx 10$ GPa (9.8 GPa from phonon dispersion analysis, while 12.2 GPa from total energy study). The FM and half-metallic properties of CrO_2 are preserved at this transition. The second structural transition is from FM o-CrO_2 to NM m-CrO_2 , which corresponds to the lattice displacement of the phonon softening at R in o-CrO_2 . The transition pressure is $P=76.0$ GPa from the phonon dispersion analysis, whereas $P=61.1$ GPa from the total energy study. The third structural transition is from NM m-CrO_2 to FM c-CrO_2 at $P=88.8$ GPa, which is accompanied by the metal to insulator transition.

Acknowledgments

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